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(54) Non-Clouding Stabilization of Water in Hydrocarbon Fractions of the Diesel and Fuel Oil Range

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NON-CLOUDING STABILIZATION OF WATER IN HYDROCARBON FRACTIONS OF THE DIESEL AND FUEL OIL RANGE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to emulsifying and stabilizing limited quantities of water in hydrocarbon fractions of everyday use and more especially in hydrocarbon fractions of the diesel oil and fuel oil range.

Technical hydrocarbon fractions of the aforementioned type are known to contain limited quantities of water amounting, for example, to between 0.5 and 10% by weight. This is generally attributable to the fact that small quantities of water are still present in pipes or storage tanks from flushing and cleaning operations, or to the fact that small quantities of water are formed as water of condensation in the storage tanks due to the moisture in the atmosphere. Since water only shows a solubility of less than about 0.5% by weight in diesel oil and fuel oil, separate phases develop therein with relatively large quantities of water. In practice, this gives rise to undesirable secondary effects in the storage of water-containing

diesel oil and fuel oil, such as for example, corrosion of the storage tanks.

An object of the present invention is to enable limited quantities of water of the order indicated above to be reliably emulsified in hydrocarbon fractions of the type mentioned and stabilized to such an extent that non-clouding, clear, single-phase liquids are obtained, even when the material is cooled to temperatures below the freezing point, for example to temperatures of -5 to -10°C.

DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

According to the invention, this object is achieved by using certain selected surfactant mixtures as emulsifiers or stabilizers for the water contents described above in the hydrocarbon fractions of the diesel oil and fuel oil range.

Accordingly, the present invention relates to the use of a multi-component surfactant mixture of at least 2 components from surfactant class A defined hereinafter, if desired in admixture with surfactants from classes B and/or C defined hereinafter, the multi-component surfactant mixture having a cloud point of from 35 to 70°C, as determined in accordance with DIN 53917, for the non-clouding emulsification and stabilization of water in hydrocarbon fractions of diesel oil and fuel oil type. More particularly, surfactant class A comprises an ethoxylate of octylphenol, nonylphenol, or isotridecylalcohol containing from 1 to 7 moles of ethylene oxide per mole of phenol or alcohol. Surfactant class B comprises a cocosalcohol ethoxylate

containing from 1 to 7 moles of ethylene oxide per mol of alcohol. Surfactant class C comprises an oleylalcohol ethoxylate containing from 1 to 7 moles of ethylene oxide per mole of alcohol.

It has been found that the problem on which the invention is based can be solved by this choice of the aforementioned specific surfactant classes A, B and C in conjunction with the definition of the hydrophilicity of the surfactant mixture used, as determined from the cloud point in accordance with DIN 53917.

In accordance with the invention, it is essential to use a mixture of at least 2 surfactants from class A. The joint use of surfactants from classes B and/or C may be desirable, but is usually not necessary. The particular choice of suitable surfactant mixture components from the above-specified classes may be made on the basis of simple measurements of the cloud point of the particular surfactant mixture to be used in accordance with DIN 53917. This standard relates to the determination of the cloud point temperature of a solution of 5 grams of the surfactant or surfactant mixture in 25 grams of an aqueous 25% by weight butyldiglycol solution. According to the invention, the cloud point of the surfactant mixture of class A and, if desired, classes B and/or C used for water emulsification and stabilization is preferably in the range of from 40 to 60°C, and more preferably in the range of from 45 to 55°C.

By selecting and combining the surfactant components according to the invention, it is possible to safely emulsify and stabilize the water present in the hydrocarbon mixture (normally in a quantity of up to about 5% by weight) using from 0.5 to 10% by weight of the surfactant mixture to form a clear, stable solution, even when the water-containing hydrocarbon frac-

tions are cooled to temperatures below room temperature and even below 0°C. In many cases, the water content of the hydrocarbon fractions of the type herein is no more than about 3% by weight. In such a case, it is possible using up to about 8% by weight, and more especially from about 1 to 6% by weight, of the surfactant mixture according to the invention, based in each case on 100 parts by weight of diesel oil or fuel oil fraction, to prepare clear solutions which retain their single-phase character at temperatures down to -4°C and lower. The above-mentioned problems involved in the practical handling of hydrocarbon fractions of the type herein are thus reliably eliminated for routine practical requirements.

As previously disclosed, at least 2 surfactants from class A are used in admixture with one another. It is of particular advantage to use an ethoxylate of the above-mentioned class A type containing 3 moles of ethylene oxide in combination with an ethoxylate of said type containing 5 moles of ethylene oxide. In this connection, particular significance is attributed to a nonylphenol ethoxylate of the above-mentioned class A type. Preferred surfactant mixtures comprise (a) from 20 to 80% by weight of nonylphenol containing about 3 moles of ethylene oxide, (b) from 20 to 80% by weight of nonylphenol containing about 5 moles of ethylene oxide, and (c) from 0 to 30% weight of oleylalcohol and/or cocosalcohol containing about 5 moles of ethylene oxide, based on the weight of the surfactant mixtures.

In a preferred embodiment, the surfactant class B component comprises a cocosalcohol having the following carbon chain distribution: C_{12}- 55% by weight, C_{14}- 25% by weight, C_{16}- 10% by weight, and C_{18}- 10% by weight.

The oleyl alcohol on which the surfactant class C component is based may have an iodine number of from 40 to 170.

The surfactant components used in accordance with this invention for stabilizing water are inexpensive, readily-available commercial products. They do not adversely affect the intended use of the correspondingly treated hydrocarbon fractions, particularly the combustion thereof for energy production.

EXAMPLES

The condition of diesel/water mixtures was assessed using various surfactant mixtures according to the invention. The following Table shows the composition of the surfactant mixture, the cloud point (DIN 53917) of the surfactant mixture, and the assessment of the appearance of the emulsion at 20°C for the following basic formulation:

(a) diesel hydrocarbon mixture	95% by weight
(b) surfactant mixture according to the invention	4% by weight
(c) water	1% by weight

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TABLE

Example No.	Composition of Surfactant Mixture	Percent by Weight	Cloud Point (DIN 53917)	Appearance of Emulsion at 20°C
1	nonylphenol-3EO nonylphenol-5EO cocosalcohol-7EO	60 30 10	48°C	clear
2	nonylphenol-3EO nonylphenol-5EO cocosalcohol-5EO	50 30 20	47°C	clear
3	nonylphenol-3EO nonylphenol-5EO oleylalcohol-7EO	50 30 20	50°C	clear
4	nonylphenol-3EO nonylphenol-6EO	20 80	50°C	clear
5	nonylphenol-3EO nonylphenol-5EO oleylalcohol-5EO	25 25 50	57°C	clear

nonylphenol-3EO, -5EO, and -6EO stands for nonylphenol containing 3, 5, and 6 moles of ethylene oxide, respectively.

cocosalcohol -5EO, -7EOP stands for cocosalcohol containing 5, and 7 moles of ethylene oxide, respectively.

Oleylalcohol -5EO, -7EO stands for oleylalcohol containing 5, and 7 moles of ethylene oxide, respectively.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. The process of using a multi-component surfactant mixture comprising at least 2 components selected from the group consisting of an ethoxylate of octylphenol, nonylphenol, and isotridecylalcohol containing from about 1 to about 7 moles of ethylene oxide, said surfactant mixture having a cloud point of from about 35°C to about 70°C as determined in accordance with DIN 53917, for the non-clouding emulsification and stabilization of water in hydrocarbon fractions of the diesel oil and fuel oil type.
2. The process as in claim 1 wherein said water is present in an amount of up to about 6% by weight, based on the weight of said hydrocarbon fractions.
3. The process as in claim 1 wherein said surfactant mixture is present in an amount of about 0.5% to about 10% by weight, based on the weight of said hydrocarbon fractions.
4. The process as in claim 1 wherein said surfactant mixture comprises an ethoxylate containing about 3 moles of ethylene oxide in admixture with an ethoxylate containing about 6 moles of ethylene oxide.
5. The process as in claim 4 wherein said ethoxylate is a nonylphenol ethoxylate.
6. The process as in claim 1 wherein said surfactant mixture includes a cocosalcohol ethoxylate containing from about 1 to about 7 moles of ethylene oxide.
7. The process as in claim 6 wherein said cocosalcohol has a carbon chain distribution of C_{12}- 55% by weight, C_{14}- 25% by weight, C_{16}- 10% by weight, and C_{18}- 10% by weight.
8. The process as in claim 1 wherein said surfactant mixture includes an oleylalcohol ethoxylate containing from about 1 to about 7 moles of ethylene oxide.
9. The process as in claim 8 wherein said oleylalcohol has an iodine number of from about 40 to about 170.
10. The process as in claim 1 wherein said surfactant mixture

comprises (a) from about 20 to about 80% by weight of nonylphenol containing about 3 moles of ethylene oxide, (b) from about 20 to about 80% by weight of nonylphenol containing about 5 moles of ethylene oxide, and (c) from 0 to about 30% by weight of oleylalcohol and/or cocosalcohol containing about 6 moles of ethylene oxide, based on the weight of said surfactant mixture.

11. The process as in claim 1 wherein said surfactant mixture has a cloud point of from about 40°C to about 80°C.

12. The process as in claim 1 wherein said water is present in an amount of up to about 3% by weight, and said surfactant mixture is present in an amount of about 1% to about 5% by weight, based on the weight of said hydrocarbon fractions.

13. A composition comprising hydrocarbon fractions of the diesel oil and fuel oil type containing up to about 5% by weight of water, and about 0.5% to about 10% by weight, based on the weight of said hydrocarbon fractions, of a multicomponent surfactant mixture comprising at least 2 components selected from the group consisting of an ethoxylate of octylphenol, nonylphenol, and isotridecylalcohol containing from about 1 to about 7 moles of ethylene oxide, said surfactant mixture having a cloud point of from about 35°C to about 70°C as determined in accordance with DIN 53917, for the non-clouding emulsification and stabilization of said water in said hydrocarbon fractions.

14. A composition as in claim 13 wherein said surfactant mixture comprises an ethoxylate containing about 3 moles of ethylene oxide in admixture with an ethoxylate containing about 6 moles of ethylene oxide.

15. A composition as in claim 14 wherein said ethoxylate is a nonylphenol ethoxylate.

16. A composition as in claim 13 wherein said surfactant mixture includes a cocosalcohol ethoxylate containing from

about 1 to about 7 moles of ethylene oxide.

17. A composition as in claim 13 wherein said surfactant mixture includes an oleylalcohol ethoxylate containing from about 1 to about 7 moles of ethylene oxide.

18. A composition as in claim 13 wherein said surfactant mixture comprises (a) from about 20 to about 80% by weight of nonylphenol containing about 3 moles of ethylene oxide, (b) from about 20 to about 80% by weight of nonylphenol containing about 5 moles of ethylene oxide, and (c) from 0 to about 30% by weight of oleylalcohol and/or cocosalcohol containing about 5 moles of ethylene oxide, based on the weight of said surfactant mixture.

19. A process of emulsifying and stabilizing up to about 5% by weight of water present in the hydrocarbon fractions of diesel oil and fuel oil, based on the weight of said hydrocarbon fractions, comprising contacting said hydrocarbon fractions with from about 0.5% to about 10% by weight, based on the weight of said hydrocarbon fractions, of a multi-component surfactant mixture comprising at least 2 components selected from the group consisting of an ethoxylate of octylphenol, nonylphenol, and isotridecylalcohol containing from about 1 to about 7 moles of ethylene oxide, said surfactant mixture having a cloud point of from about 35°C to about 70°C as determined in accordance with DIN 53817, whereby said diesel oil and fuel oil is rendered non-cloudy and less corrosive to storage tanks.

20. The process as in claim 19 wherein said surfactant mixture is present in an amount of about 0.5% to about 10% by weight, based on the weight of said hydrocarbon fractions.

21. The process as in claim 19 wherein said surfactant mixture comprises an ethoxylate containing about 3 moles of ethylene oxide in admixture with an ethoxylate containing about 5 moles of ethylene oxide.

22. The process as in claim 21 wherein said ethoxylate is a nonylphenol ethoxylate.

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23. The process as in claim 19 wherein said surfactant mixture includes a cocosalcohol ethoxylate containing from about 1 to about 7 moles of ethylene oxide.

24. The process as in claim 23 wherein said cocosalcohol has a carbon chain distribution of C_{12}- 55% by weight, C_{14}- 25% by weight, C_{16}- 10% by weight, and C_{18}- 10% by weight.

25. The process as in claim 19 wherein said surfactant mixture includes an oleylalcohol ethoxylate containing from about 1 to about 7 moles of ethylene oxide.

26. The process as in claim 25 wherein said oleylalcohol has an iodine number of from about 40 to about 170.

27. The process as in claim 19 wherein said surfactant mixture comprises (a) from about 20 to about 60% by weight of nonylphenol containing about 3 moles of ethylene oxide, (b) from about 20 to about 80% by weight of nonylphenol containing about 5moles of ethylene oxide, and (c) from 0 to about 30% by weight of oleylalcohol and/or cocosalcohol containing about 5 moles of ethylene oxide, based on the weight of said surfactant mixture.

28. The process as in claim 19 wherein said surfactant mixture has a cloud point of from about 40°C to about 60°C.

29. The process as in claim 19 wherein said water is present in an amount of up to about 3% by weight, and said surfactant mixture is present in an amount of about 1% to about 5% by weight, based on the weight of said hydrocarbon fractions.

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ABSTRACT OF THE DISCLOSURE

The process of using a multi-component surfactant mixture comprising at least 2 components selected from the group consisting of an ethoxylate of octylphenol, nonylphenol, and isotridecylalcohol containing from about 1 to about 7 moles of ethylene oxide, wherein the surfactant mixture has a cloud point of from about 35°C to about 70°C as determined in accordance with DIN 53917, for the non-clouding emulsification and stabilization of water in hydrocarbon fractions of the diesel oil and fuel oil type.